Effects of Synthesis Methods on the Performance of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$

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The layered cathode material $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ has been synthesized by sol-gel method ,solid-state method and carbonate co-precipitation method, respectively. XRD, SEM, CV, EIS and electrochemical measurements were used to characterize the samples synthesized via different synthetic routes. The results show that the difference in preparation methods results in the difference in the structure, morphology of the prepared materials and electrochemical performance. $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ prepared by the sol-gel method exhibited higher discharge capacity than $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ prepared by the other two methods, its initial specific discharge capacity was 191.8 mAh/g (2.3-4.6V, 0.1*C* rate). However, the sample prepared by the other two methods, it exhibited the capacity retention when compared to the sample prepared by the other two methods, it exhibited the capacity retentions of 93.0% at 0.2C after 50 cycles.

Keywords: lithium batteries, LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂, synthesis method, electrochemical performance

1. INTRODUCTION

LiCoO₂ is the most widely used commercial cathode material for lithium secondary batterie, but its application is limited because of the scarce cobal resources, high prices and a certain degree of toxicity. Therefore, the researchers put their attention to the other transition metal <u>oxide</u>s, such as LiNiO₂, and LiMn₂O₄. However, LiNiO₂ suffers from safety and stability problems[1], LiMn₂O₄ has serious capacity fading problem during cycling, especially under high temperature[2]. Layer-structured LiNi_xCo_yMn_{1-x-y}O₂ cathode material has attracted much attention for it integrates the features of LiCoO₂, LiNiO₂, and LiMn₂O₄ with structural stability, high capacity, low cost, safety, and so on. Thus, it became one of the most commercialization potential cathode material[3,4].LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ has been studied extensively. However, compared with LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ with less expensive Co content can reduce the material cost and environmental pollution caused by production process. Ni contributed to more for the capacity, the higher the relative concentration of nickel in the material, the higher the specific capacity. While the increase of Mn concentration elevates the safety performance .Thus it is a cathode material that deserves more research works. However, this kind of material suffers from such drawbacks as shortage of cycling performance and poor rate capacities[5-7].

The microstructure, surface morphology and electrochemical properties of the cathode materials are fairly closely linked with the synthesis methods. The methods of preparing $LiNi_xCo_yMn_{1-x-y}O_2$ powders include co-precipitate method[8], hydrothermal method[9], solid-state method[10], sol-gel method[11], spray drying process[12], rheological phase method[13], etc. In this paper, we synthesized $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ powders via three different methods, solid-state method, sol-gel method and carbonate co-precipitation method. In addition, the morphological and electrochemical differences of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ prepared by different methods were investigated.

2. EXPERIMENTAL

2.1. Synthesis of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ powders by solid-state method

A stoichiometric amount of LiCH₃COO·2H₂O, Ni(CH₃COO)₂·4H₂O, Mn(CH₃COO)₂·4H₂O, Co (CH₃COO)₂·4H₂O were mixed with the citric acid used as a fuel, and then grind them fully in an agate mortar. The initial product was dried at 120°C for 8h and then heated at 500°C for 6h to eliminate the organic residues. The final powders (denoted as SP) were gained by a thorough grounding step, a final calcining at 850°C for 20h in air and followed by quenching to room temperature.

2.2. Synthesis by sol-gel method

LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ powders were prepared via a sol-gel process using citric acid as chelating agent. A stoichiometric amount of LiCH₃COO·2H₂O, Ni(CH₃COO)₂·4H₂O, Mn(CH₃COO)₂·4H₂O and Co (CH₃COO)₂·4H₂O were dissolved in distilled water, and then added the aqueous solution of citric acid into the mixture metal solution. The molar ratio of citric acid to total metal ions was unity. The pH of the solution was adjusted in the range 7–8 by adding ammonium hydroxide. The reagent solution was stirred continuously at 80°C until form homogeneous sol and gel. The resulting gel was dried at 120°C for 8h and then heated at 500°C for 6h to eliminate the organic residues. The final powders (denoted as SG) were gained by a thorough grounding step, a final calcining at 850°C for 20h in air and followed by quenching to room temperature.

2.3. Synthesis by carbonate co-precipitation method

For preparing transition metal carbonate powder $Ni_{0.4}Co_{0.2}Mn_{0.4}CO_3$, we used LiOH·H₂O, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, Co $(CH_3COO)_2 \cdot 4H_2O$ and Na2CO3 as the starting

materials. The stoichiometric amounts of Ni(CH₃COO)₂·4H₂O, Mn(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O were dissolved together in distilled water in beaker A (Solution A). The proper amount of Na₂CO₃ also dissolved in distilled water in beaker B (Solution B). Each solution was slowly poured into another beaker (Solution A+ B) with heating at 80 °C until sediment formed. The pH value of the coprecipitation solution was maintained via carefully adding ammonia. The obtained Ni_{0.4}CO_{0.2}Mn_{0.4}CO₃ complex after washing and drying was mixed with LiOH·H₂O and calcined at 500 °C for 6 h in air. The final powders (denoted as CP) were gained by a thorough grounding step, a final calcining at 850°C for 20h in air and followed by quenching to room temperature.

The X-ray diffraction (XRD) with Cu K α radiation operated at 40kV and 40mA was used to analyze the crystalline structure of samples. The scan data were in the 2 θ range from 10° to 90° in step of 4°/min. The size and morphology of the sample were visualized using SEM performed on S4800 microscope with 5 kV.

Electrochemical experiments were performed using two-electrode coin cells. The composite cathodes were made by dispersing active material (80 wt.%), acetylene black (12 wt.%), and PVDF (8 wt.%) to form a slurry, The slurry was pasted onto Al foil then pressed at 10MPa and dried at 120°C for 10h in a vacuum oven. The CR2032 coin cells were assembled in an argon-filled glove box using lithium metal as the counter electrode, Celgard 2325 as the separator, and 1 M LiPF6 in 1:1 EC:DMC solution as the electrolyte. Charge–discharge performance of the cells was evaluated within different cut-off voltages and at different discharge rates at room temperature using LAND CT2001A electrochemical test instrument.

The cyclic voltammogram (CV) curves were obtained between the cut-off voltage ranges of 2.5-4.8V on an IM6 Electrochemical workstation at a scan rate of 0.1mV/s.

Electrochemical impedance spectroscopy (EIS) was measured with IM6 Electrochemical workstation. The ac perturbation signal was ± 5 mV and the frequency range was from 0.05Hz~ 100 kHz.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ (SG, CP and SP). All of the peaks can be indexed on the basis of a layered structure of α -NaFeO₂ structure (space group: R-3m). The clear split of the (006)/(102) peaks and(018)/(110) peaks for SG and CP samples manifest the formation of well hexagonal layered ordering structure[14]. However, careful examination of the diffraction pattern for the SP sample shows the absence of splitting for (006)/(012) reflections indicating lack of a perfectly layered structure. The lattice parameters of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ (SG, CP and SP) cathode materials are illustrated in Table 1. The integrated intensity ratio of the (003) to (104) in the XRD patterns is sensitive to the degree of cation mixing in lattice[15] and a value of I₍₀₀₃₎/I₍₁₀₄₎ <1.2 is an indication of undesirable cation mixing. So, good electrochemical performance can be expected for SG and CP samples. But the integrated intensity ratio of (003) to (104) peak of SP sample is 1.05, indicating larger cation mixing. The c/a ratio > 4.96 also reveals the well-defined layered structure, the higher value of c/a, the better well-defined layered structure [16]. The same conclusion have been obtained by comparing the value of c/a of SG, CP and SP samples.



Figure 1. XRD patterns of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ prepared by different methods.

Table 1. Lattice parameters of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ prepared by different methods

sample	a(Å)	c(Å)	c/a	I ₍₀₀₃₎ /I ₍₁₀₄₎
SG	2.87509	14.26794	4.963	1.24
СР	2.87212	14.26661	4.967	1.25
SP	2.87504	14.25867	4.959	1.04

SEM micrographs of the three samples of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (SP, SG and CP) are illustrated in Fig.2. The particle prepared by sol-gel method is composed of very uniform and small nanocrystallites with particle size about 200–400 nm. SG powder with a high surface area would have high surface reactivity.



Figure 2. SEM micrographs of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ samples: (a) sol-gel method, (b) co-precipitation method and (c) solid-state method

SP-sample consists of particles with no characteristic morphology and most grains are badly aggregated, unfortunately, this can lead to descend of electrochemical capability of the sample. The size of the particle prepared by carbonate co-precipitation methods is about 1-2 μ m, Dahn and co-workers [17] recently reported that larger particles result in a higher tap density. As is well known, the distinctions of SP, SG and CP in size, morphology and surface area would lead to differences in their electrochemical performance.

Fig.3 (a) shows the initial charge-discharge curves of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ (SG, CP and SP) in the range of 2.5–4.6V at 0.1C rate at room temperature. As can be seen from the figures, the obtained SG, CP and SP cathodes can deliver discharge capacities of 191.8, 189.5 and167.6mAh/g, respectively, with initial coulombic efficiencies of 92.93% \times 83.33% and 83.25%. As we can see, for all of the samples, at the beginning of the charging process, the voltage suddenly increases to about 3.7V and holds at 3.7-4.0V, and then significantly rises to 4.6 V in the case of sample SG. However, in the case of sample CP and SP, it increases at first to 4.5V rapidly, and then gradually climbs up to 4.6V, accompanied a narrow plateau around 4.5V. Fig.3 (b) shows the discharge curves and cycling performance of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ (SG, CP and SP) in the range of 2.0-4.6V at various rates from 0.2 C to 2.5C. The as seen in Fig.3 (b), the rate was increased from 0.2 to 2.5C stepwise, the sample SG shows higher discharge capacity than the other two samples. That is because the nano-sized particles synthesized by sol–gel method can greatly reduce the diffusion paths for Li ions, the insertion and de-insertion of the Li⁺ in this material are expected to be faster thus enhancing the discharge capacity of this sample.



Figure 3. (a)Initial charge-discharge curves of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ samples synthesized by different methods; (b)Cycle performance of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ electrode prepared by different methods at different discharge rates.

In order to explore the differences among SG sample, CP sample and SP sample during initial charge-discharge process, we carried out cyclic voltammetry in the range 2.5-4.8V with a scanning rate of 0.1 mV/s as shown in Fig. 4. The curves of all the samples have two anodic peaks and two cathodic peaks, the cathodic peaks for the three samples of the first cycle center around 4.0 and 4.6V which

attribute to the oxidation of Ni²⁺/Ni⁴⁺ and Co³⁺/Co⁴⁺ couple, and the corresponding anodic peaks center around 3.6 and 4.5 V, respectively[18]. But, compared with SG sample, a large irreversible anodic peak above 4.5V can be found for the CP and SP samples. Not coincidentally, the irreversible anodic peak correspond to the plateau around 4.5V in the initial charge-discharge curves. That is why, the sample SG shows higher initial coulombic efficienciey than the other two samples. The reason for the existence of the irreversible anodic peak above 4.5V may have something to do with the preparation method, we think that its origin is in fact correlated to the true chemical composition of sample. CP sample and SP sample should be considered as a solid solution of a layered compound of Li-Ni-Mn-Co-O with Li₂MnO₃[19], such as LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂-Li₂MnO₃ since the plateau around 4.5V was usually observed in the solid solution of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂-Li₂MnO₃ [20]. On the other hand, this smaller potential difference indicates the weaker electrode polarization is, which ensures reduced capacity fade during cycling[21]. It is quite clear that the potential difference of the major peak of CP sample is minimal, it would show the best capacity retention.



Figure 4. Cyclic voltammogram curves of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ samples prepared by different methods

Fig. 5 represented the capacity retention of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ (SG, CP and SP) at 0.2C between 2.0 and 4.6 V at room temperature.



Figure 5. Cycling performance of LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ samples synthesized by different methods

The first discharge capacities of SG sample, CP sample and SP sample are 185.6, 174.8 and 144.6mAh/g, with the capacity retention ratio of 90.9% \$\sqrt{93.0\%}\$ and 85.5% after 50cycles, respectively. The CP electrode exhibits better cycling performance than SG sample, this is because the increased surface area of the larger particles prepared by sol-gel method, increases the insulating film formation due to increased decomposition reactions with the electrolyte during cycling. This insulating surface film would block the direct interconnections between the active particles and the electrolyte, and this would deteriorate the charge transfer reactions between the active particles and the current collector, causing an increase in charge transfer resistance. The SP sample has maximum cation mixing among all the three methods and shows poor electrochemical performance.

In order to further explain the difference in electrochemical performances of the $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ samples synthesized by different methods, EIS measurements were carried out on SG sample and CP sample at the terminated voltage of 4.0V after 1 and 50 cycles, respectively. Fig. 6(a) illustrates the EIS curves of the test cells with SG sample and CP sample. The equivalent circuit is also shown in Fig. 6 (b).We can see the EIS curves consist of two semicircles in high frequency range and a quasi-linear line (W) in low frequency range, in which the first semicircle in high frequency range reflects the lithium-ion migration resistance through the interface between the surface layer of the material particles and the electrolyte (Rf); the other arc in intermediate frequency range reflects charge-transfer resistance (Rct).



Figure 6. (a) EIS curves of SG sample and CP sample; (b) equivalent circuit of EIS

The quasi-linear part at low frequency region is related to the Warburg contribution characteristic of the lithium-ion diffusion through the bulk into the active material. The Z' intercept of the first semicircle on the real axis is related to the bulk resistance (Rs) of the electrolyte[22]. In Fig.6, the first semicircle has virtually no change during cycling. However, the second semicircle increases substantially during cycling. The diameter of the second semicircle of SG sample is 55.1 Ω at the first

cycle then enlarges drastically to 110Ω at the 50th cycle. By contrast, the diameter of the second semicircle of CP sample only increase from 10.6Ω at the first cycle to 52.3Ω at the 50th cycle. This showed that the charge transfer resistance of SG sample is higher than that of CP sample. Experimental results have validated the above conclusion that we've got in charge-discharge test.

4. CONCLUSION

 $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ has been prepared by three different synthetic routes, sol-gel method, solid-state method and carbonate co-precipitation method, respectively. The difference in preparation method leads to the difference in morphology and the difference in the electrochemical performance. The $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ prepared by sol-gel method delivered a higher capacity than electrode prepared by two other methods owing to shorter diffusion length and higher surface area. whereas CP-sample showed better capacity retention than the other two samples due to lower surface area and hence decreased side reactions with the electrolyte.

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